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ANALYTICAL REFERENCE SERVICE. REPORT ON SAMPLE TYPE III

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

March 1958

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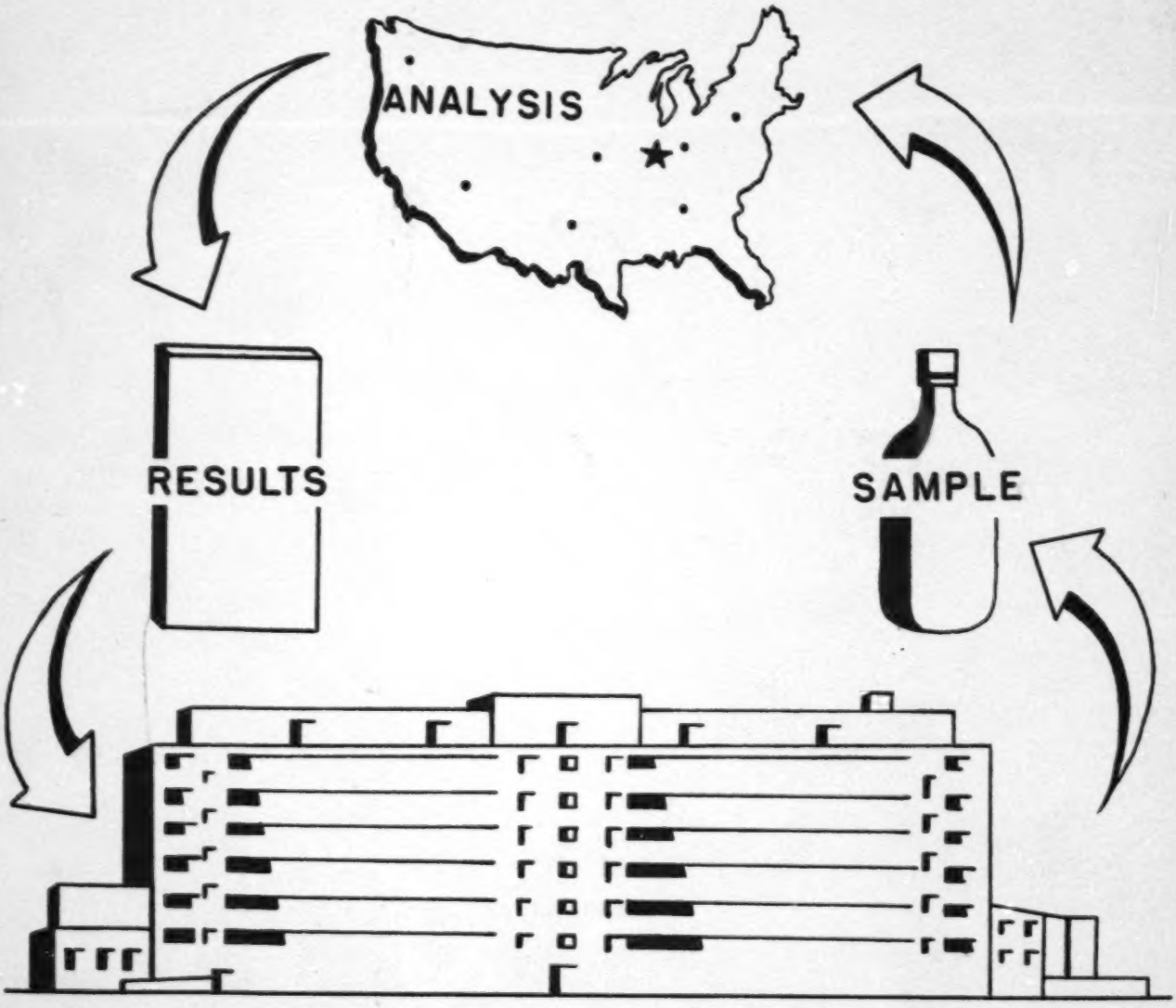
MARCH, 1958



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ANALYTICAL REFERENCE SERVICE

INTRODUCTION

The Analytical Reference Service conducted by the Sanitary Engineering Center has as its primary goal the evaluation of laboratory methods in the field of sanitary engineering. The Reference Service itself is a voluntary association of member organizations responsible for the conduct of laboratory programs. The evaluations are obtained by the cooperative efforts of the members in the analysis of identical samples.

This mechanism provides:

1. A statistical evaluation of procedures, including precision and accuracy.

2. An opportunity for a participant to compare his laboratory procedures and results with other laboratories having similar responsibilities.

3. An exchange of information regarding weaknesses of currently approved methods.

4. Evidence regarding methods requiring further development or perhaps entirely new approaches.

5. A framework for broad-scale evaluation of new analytical methods.

PLAN OF OPERATION

Initially, efforts are being directed toward the chemical examination of water. The scope of the program will be broadened gradually to include other types of examinations and other media.

Using the most refined grade of chemicals available, samples are prepared containing measured amounts of the desired constituent. Decisions as to the qualitative makeup of any particular sample follow suggestions from the members and from the staff of the Sanitary Engineering Center.

After a sample is designed and prepared, a notice announcing its availability and qualitative makeup is sent with a self-addressed reply card to member organizations. An affirmative reply initiates immediate shipment of a portion of the described sample. Results are requested within some reasonable period, usually sixty days.

REPORTING OF RESULTS AND COMMENTS

Data are returned to the Sanitary Engineering Center on forms supplied with the sample. Space is provided on the forms for numerical values and a narrative critique of analytical procedures used.

The results obtained by the cooperating laboratories are compiled as in the accompanying report. From examination of the combined data it is hoped that reliable estimates may be made of the accuracy and precision of the methods employed.

All laboratories are strongly encouraged to supply comments on the analytical methods they use. A complete log of pertinent details, including difficulties, modifications, sources of error, and other factors, is extremely valuable. Such a compilation of comments represents an exchange of ideas and opinions that is a significant part of the final report.

H. P. Kramer

H. P. Kramer
Chief, Training Program

ANALYTICAL REFERENCE SERVICE

MEMBERS AS OF JANUARY 1, 1958

State Agencies

Arizona State Department of Health
Arkansas State Board of Health
California State Department of Health (Berkeley)
California State Department of Health (Los Angeles)
Colorado State Department of Public Health
Illinois State Water Survey Division
Kentucky State Department of Public Health
Louisiana State Department of Health
Maryland State Department of Health
Maryland Water Pollution Control Commission
Michigan State Department of Health
Minnesota State Department of Health*
Missouri Department of Public Health and Welfare
Montana State Board of Health
Nebraska State Department of Health*
New Hampshire Water Pollution Commission
New Jersey State Department of Health
New Mexico State Department of Public Health
New York State Conservation Department
New York State Department of Health
North Carolina State Stream Sanitation Committee
Ohio State Department of Health
Oregon State Board of Health
Pennsylvania State Department of Health
South Carolina State Water Pollution Control Authority
South Dakota State Board of Health
Tennessee State Department of Public Health
Texas State Department of Health
Utah State Department of Health
Vermont Department of Health
Vermont Water Conservation Board
Virginia Water Control Board
Washington State Department of Health*
West Virginia State Water Commission

*New Members since July 1, 1957

Federal Agencies

Army Chemical Center, Edgewood, Maryland
Sanitary Engineering Division, 13th Naval District
U.S. Geological Survey, Department of the Interior
Columbus, Ohio
Sacramento, Califprnia
Washington, D. C.

Universities

Rutgers University, Department of Sanitation
Purdue University, Department of Chemistry

PARTICIPANTS IN THIS STUDY OF SAMPLE TYPE III

(Distributed March, 1957)

Arizona State Department of Health
Arkansas State Board of Health
California State Department of Health (Berkeley)
California State Department of Health (Los Angeles)
Colorado State Department of Public Health
Illinois State Water Survey Division
Kentucky State Department of Public Health
Louisiana State Department of Health
Maryland State Department of Health
Michigan State Department of Health
Missouri Department of Public Health and Welfare
Montana State Board of Health
New Jersey State Department of Health
New Mexico State Department of Public Health
New York State Department of Health
Ohio State Department of Health
Oregon State Board of Health
Pennsylvania State Department of Health
South Dakota State Board of Health
Tennessee State Department of Public Health
Texas State Department of Health
Vermont Department of Health
Division of Dental Public Health
Public Health Service Laboratory, Bethesda, Maryland
Army Chemical Center, Edgewood, Maryland
U. S. Geological Survey, Department of the Interior
Columbus, Ohio
Sacramento, California
Washington, D. C.

SAMPLE TYPE III (Fluoride)

PURPOSE OF THIS STUDY

At the present time, approximately 1500 communities serving thirty-three million people in the United States are fluoridating their water supplies. Since strict control of the fluoridating chemical is required, fluoride determinations of raw and finished water have become routine in many laboratories.

Unfortunately, the methods available for fluoride determinations in water are more difficult than other routine procedures. Much work has been done during the past decade on the design of simpler and more accurate procedures for fluorides. The Eriochrome Cyanice R method* for fluoride was chosen for evaluation by the Analytical Reference Service because it appeared to have certain advantages over other methods in current use. The decision to evaluate the ECR method was not made until after the procedure had been well-screened in this laboratory. In this study determinations were performed on three different solutions of known composition, comparing the ECR with current routine methods. This was intended to produce sufficient data for valid judgment as to the effectiveness of the ECR method.

PREPARATION OF SAMPLE

Substrate:

Distilled water passed through a de-ionizing column was used.

Chemicals:

All reagents were ACS Reagent Grade taken from freshly opened bottles.

Composition:

Sample Type III is a family of three separate solutions designated A, B, and C as follows:

*Rapid Spectrophotometric Determination of Fluoride with Zirconium - Eriochrome Cyanine R Lake, Stephen Megregian.
ANALYTICAL CHEMISTRY, Volume 26, Page 1161, (1954).

Constituent	Solution A	Solution B	Solution C
Fluoride	0.92 mg/l	0.76 mg/l	0.87 mg/l
Alkalinity	0	300	300
Sulfate	0	200	100
Aluminum	0	2.0	0
Hexametaphosphate	0	0	2.5

Solution A served as the control, no interfering substances being added. Unsatisfactory results obtained with solution A would indicate inadequate methods or faulty application. The effect of distillation upon the procedure employed becomes evident when it is the only variable, as may be observed by comparing the results obtained from solution A on the distilled and nondistilled bases.

Solution B contained sulfate and aluminum as the principal interferences. The interferences were investigated because the ECR method contains a relatively simple procedure for eliminating errors due to these materials. The resulting data should indicate the effectiveness of the ECR correction procedures and also illustrate the influence of these interferences on results from other methods. Distillation was requested for solution B because it is the means of eliminating sulfate and aluminum when methods other than the ECR are used.

Solution C contained hexametaphosphate as an interference. This material is a frequent and serious source of error common to all fluoride methods, distillation being the only method currently available to over come it. Solution C data indicate the relative effects of hexametaphosphate on the compared fluoride methods.

Both solutions B and C contained 300 mg/l of alkalinity, added as sodium bicarbonate, so that the solutions would more nearly duplicate natural samples. No provisions were made for evaluation of the alkalinity as an interfering material.

TREATMENT OF THE DATA

It was requested that all results be reported to the second decimal place. For the photometric procedure this is reasonable. For the visual methods, however, the "second decimal" becomes a subjective number. If the reported values did not include the second digit it was assumed to be zero; for example, a result reported as 0.9 was rated as 0.90.

In this study, twenty-seven laboratories performed 150 distillations and reported 914 analytical results. Such an abundance of data could lend

itself to intensive statistical treatment, but this report includes only the common statistical measures. The data are available for those who desire to study them in more detail.

The standard deviation in the raw data was calculated from the difference between the reported values and the amount of fluoride actually added. All reported values greater than two standard deviations were then rejected, and the standard deviation recalculated. This refined standard deviation more nearly reflects the accuracy of the analytical methods employed in this study, as approximately ninety-five per cent of the reported values are retained, but those showing gross errors are eliminated.

Authorities in the field of fluoridation have generally agreed that an acceptable fluoride method should be capable of producing an accuracy of $\pm$ 0.10 mg/l at a concentration level of 1.00 mg/l. This recommendation is used throughout this report as a baseline and is used especially in the bar charts as a standard of performance.

LABORATORY METHODS AND EQUIPMENT

Of the twenty-seven laboratories participating in this study, twenty-six stated that they analyzed fluoride samples routinely. The data obtained, therefore, are based on work by analysts familiar with one or more fluoride methods. The routine methods specified by the participants were as follows:

Method	Users
Scott-Sanchis	12
Megregian-Maier	9
Lamar	1
Thorium nitrate	1
Modified ECR	1
Not identified	1
No comparison performed	2

In the present report these methods will be referred to as "other" methods. The Scott-Sanchis and Megregian-Maier methods are given special consideration because the number of laboratories using these methods was sufficient to allow statistical treatment.

All of the participating organizations possessed photo-electric equipment. The types are listed below:

Instrument	Users
Beckman, Model B	12
Beckman, DU	7

Instrument	Users
Coleman, Model 6-A	1
Coleman, Model 11	1
Coleman, Model 14	2
Coleman, Model ?	1
Bausch & Lomb, Spectronic 20	1
Klett Summerson	1
Evelyn	1

It is assumed in this report that the type of instrument used has no effect upon the results obtained.

DISCUSSION OF RESULTS

SOLUTION A (0.92 mg/l F)

With Solution A, which contained no interferences, a large majority performed very well on the nondistilled aliquots. With the ECR procedure, twenty-two laboratories obtained results within ± 0.10 mg/l of the true value. By the other methods, twenty-four laboratories obtained values within ± 0.10 mg/l. The arithmetic mean of all ECR values without distillation was 0.95 mg/l, as compared to 0.91 mg/l for all other methods. The standard deviations for both groups of data were 0.062 and 0.064 mg/l respectively. These figures indicate that in the absence of interfering substances the average laboratory can routinely produce results within the ± 0.10 mg/l limit, employing either the ECR or older and more commonly used methods. The Megregian-Maier photometric procedure (used by nine laboratories) gave a standard deviation of 0.073 mg/l, while the visual Scott-Sanchis method (employed by twelve laboratories) gave a standard deviation of 0.023 mg/l.

When Solution A was distilled, the data were decidedly different. Of the twenty-five laboratories submitting results on the ECR procedure, sixteen obtained within ± 0.10 mg/l of the true value. With the other methods only thirteen of the twenty-three reporting laboratories fell within this limit. The arithmetic mean for the ECR method was 1.02 mg/l as compared to 1.00 mg/l for the other methods, and the standard deviations were respectively 0.137 and 0.158 mg/l. It is observed that the Scott-Sanchis method is less affected by distillation than is the Megregian-Maier method, their standard deviations being 0.070 and 0.160 mg/l in the order named.

STATISTICAL SUMMARY, SOLUTION A

Method	Nondistilled			Distilled		
	No. of Analyses	Arith Mean	Standard Deviation	No. of Analyses	Arith Mean	Standard Deviation
ECR	81	0.95	0.062	75	1.02	0.137
Other	78	0.91	0.064	72	1.00	0.158
M & M	27	0.87	0.073	24	1.01	0.160
S & S	36	0.93	0.023	36	0.94	0.070

The major conclusions from the data obtained on Solution A are:

1. Using either the ECR or conventional methods, fluoride can be measured in the absence of interfering substances to within ± 0.10 mg/l at the 1.0 mg/l level.

2. The distillation procedures in current use constitute a serious source of error in fluoride measurement, the standard deviation being approximately doubled.

3. Of the three methods employed (ECR, Scott-Sanchis and Megregian-Maier) for which suffificient data are available for statistical analysis, the Scott-Sanchis method gives the best results both on nondistilled and distilled samples.

SOLUTION B (0.76 mg/l F, 200 mg/l SO_4, 2.0 mg/l Al)

Solution B contained two interferences, sulfate at a concentration of 200 mg/l and aluminum at a concentration of 2.0 mg/l. The ECR procedure proposes to correct for these interferences without distillation. With twenty-seven laboratories performing the analysis employing the correction procedures, the ECR gave an arithmetic mean of 0.67 mg/l, only ten groups reporting values within the desired limits. The standard deviation was 0.215 mg/l.

For the other methods on the undistilled basis, the arithmetic mean was 0.63 mg/l with twenty-one of twenty-five laboratories reporting deviations greater than ± 0.10 mg/l from the true value. The standard deviation obtained with these methods (undistilled) was significantly lower, being 0.172 mg/l. The Megregian-Maier gave a standard deviation of 0.202 mg/l and the Scott-Sanchis 0.154 mg/l. Even without distillation, both of these methods yielded standard deviations less than that of the ECR method.

Examination of the raw data indicates that the ECR method and its correction procedures could yield accurate results, but that some analysts experienced considerable difficulty with the technique.

With the distilled samples, both the ECR and the other methods gave improved results. The ECR data yielded an arithmetic mean of 0.84 mg/l, with a standard deviation of 0.175 mg/l. The arithmetic mean of all other methods was 0.76 mg/l with a standard deviation of 0.139 mg/l. Again, the Scott-Sanchis method was statistically superior to the Megregian-Maier procedure, the standard deviations being 0.106 and 0.153 mg/l respectively.

STATISTICAL SUMMARY, SOLUTION B

Method	Nondistilled			Distilled		
	No. of Analyses	Arith Mean	Standard Deviation	No. of Analyses	Arith Mean	Standard Deviation
ECR	81	0.67	0.215	75	0.84	0.175
Other	78	0.63	0.172	72	0.76	0.139
M & M	27	0.52	0.202	24	0.72	0.153
S & S	36	0.63	0.154	33	0.80	0.106

The conclusions reached are:

1. The correction procedures for the sulfate and the aluminum interferences on the ECR method are workable but tend to give low results.

2. Distillation for removal of sulfate and of aluminum interferences is advisable when either the Scott-Sanchis or Megregian-Maier procedure is used.

3. Distillation procedures in current use constitute a source of error to all of the fluoride methods studied.

SOLUTION C (0.87 mg/l F, 2.5 mg/l $[NaPO_3]_6$)

Solution C contained as the interference 2.5 mg/l of hexametaphosphate. This material is not as likely to occur in domestic waters as is aluminum or sulfate, but because of its widespread use in washing compounds it is likely to occur in raw surface water or on laboratory glassware used in fluoride analysis.

No correction procedure is offered for hexametaphosphate other than distillation. The results obtained on the undistilled portion of Solution C for the ECR and other methods serve as an index of the error introduced by this interference. For both the ECR and other methods the arithmetic mean was 1.02 mg/l. The standard deviation for the ECR method was 0.165 mg/l and for the Megregian-Maier method 0.348 mg/l. This indicates that the interference due to the hexametaphosphate is considerably greater in the case of the Megregian-Maier method. The Scott-Sanchis method, however, again yielded greater accuracy, its standard deviation being only 0.099 mg/l.

The same pattern persists for the Solution C distilled as for distilled portions of Solutions A and B. The arithmetic means with both the ECR and other methods are within the $\pm$ 0.10 mg/l, but the standard deviations indicate considerable variation in the individual results. The standard deviation for the ECR method following distillation was 0.150 mg/l as compared to 0.130 mg/l for the other methods. The Megregian-Maier method yielded a standard deviation of 0.202 mg/l as against 0.086 mg/l for the Scott-Sanchis.

STATISTICAL SUMMARY, SOLUTION C

Method	Nondistilled			Distilled		
	No. of Analyses	Arith Mean	Standard Deviation	No. of Analyses	Arith Mean	Standard Deviation
ECR	81	1.02	0.165	78	0.96	0.150
Other	78	1.02	0.230	72	0.97	0.131
M & M	27	1.18	0.348	24	1.04	0.202
S & S	36	0.89	0.099	36	0.92	0.086

The main conclusion reached from this set of data is that the Scott-Sanchis method is affected less by hexametaphosphate interference than are the other procedures.

SUMMARY OF RESULTS

COMPARISON OF REPLICATE VALUES
SOLUTION A -0.92 mg/l FLUORIDE
NON DISTILLED

Lab. No.	ECR METHOD Replicate Values	ECR METHOD Average	OTHER METHODS Replicate Values	OTHER METHODS Average	Method
1	0.91		0.91		
	0.92	0.91	0.91	0.92	Megregian-Maier
	0.91		0.94		
2	0.90		0.95		
	0.90	0.91	0.95	0.95	Scott-Sanchis
	0.94		0.95		
3	0.85		0.90		
	0.85	0.85	0.94	0.93	Scott-Sanchis
	0.85		0.94		
4	1.41		0.87		
	0.93	1.09	1.14	1.01	Megregian-Maier
	0.93		1.02		
5	0.95		0.95		
	0.96	0.96	0.98	0.97	Megregian-Maier
	0.97		0.98		
6	0.92		0.95		
	0.90	0.91	0.95	0.95	Scott-Sanchis
	0.92		0.95		
7	0.89		0.90*		
	0.89	0.88	0.90*	0.90*	Scott-Sanchis
	0.85		0.90*		
8	0.96		0.95		
	0.92	0.93	0.93	0.93	Scott-Sanchis
	0.90		0.92		
9	1.00		1.00		
	1.00	1.01	1.00	1.00	Scott-Sanchis
	1.04		1.00		
10	0.97		1.00		
	0.92	0.94	1.00	1.00	Megregian-Maier
	0.94		1.00		
11	0.91		0.90		
	0.87	0.89	0.90	0.90	Scott-Sanchis
	0.90		0.90		
12	1.10		1.04		
	1.08	1.06	0.97	1.00	Megregian-Maier
	1.00		1.00		
13	0.90		1.00		
	0.90	0.90	0.95	0.95	Lamar
	0.91		0.90		

*Second number estimated to be zero

Lab. No.	Replicate Values	Average	Replicate Values	Average	Method
14	0.98		0.93		
	0.98	0.98	0.92	0.92	Scott-Sanchis
	0.97		0.93		
15	0.81		0.92		
	0.89	0.84	0.89	0.90	Scott-Sanchis
	0.82		0.89		
16	0.94		0.95		
	0.94	0.95	0.96	0.95	Megregian-Maier
	0.96		0.93		
17	0.79		0.80*		
	0.81	0.80	0.80*	0.80*	Not Identified
	0.79		0.80*		
18	0.96		0.97		
	0.94	0.95	0.95	0.96	Megregian-Maier
	0.94		0.97		
19	0.90		0.90*		
	0.94	0.93	0.90*	0.90*	Scott-Sanchis
	0.97		0.90*		
	0.92				
20	1.15		0.20		
	1.20	1.17	0.10	0.13	Megregian-Maier
	1.15		0.10		
21	0.89		0.93		
	0.89	0.89	0.90	0.91	Megregian-Maier
	0.88		0.90		
22	1.04		1.08		
	1.04	1.04	1.06	1.08	Thorium Nitrate
	1.03		1.10		
23	0.92		0.90		
	0.96	0.92	0.95	0.93	Scott-Sanchis
	0.88		0.95		
24	0.94		0.90		
	0.95	0.94	0.95	0.93	Modified ECR
	----		0.95		
25	0.99		----		
	0.98	0.98	----	----	None
	0.98		----		
26	1.00*		0.90		
	0.97	0.98	0.95	0.92	Scott-Sanchis
	0.97		0.92		
27	1.00		----		
	0.96	0.99	----	----	None
	1.00		----		
SEC	0.94		0.91		
	0.97	0.96	0.89	0.91	Megregian-Maier
	0.96		0.92		

*Second number estimated to be zero

COMPARISON OF REPLICATE VALUES
SOLUTION A - 0.92 mg/l FLUORIDE
DISTILLED

Lab. No.	ECR METHOD Replicate Values	ECR METHOD Average	OTHER METHODS Replicate Values	OTHER METHODS Average	OTHER METHODS Method
1	0.96 0.90 0.90	0.92	0.96 0.90 0.84	0.90	Megregian-Maier
2	0.86 0.83 0.83	0.84	0.88 0.88 0.88	0.88	Scott-Sanchis
3	0.85 0.85 0.85	0.85	0.74 0.80 0.83	0.79	Scott-Sanchis
4	0.93 1.86 2.31	1.70	2.01 1.86 1.71	1.86	Megregian-Maier
5	0.93 0.96 1.08	0.99	0.96 0.96 0.88	0.93	Megregian-Maier
6	0.92 0.92 0.92	0.92	0.95 0.95 0.95	0.95	Scott-Sanchis
7	1.36 1.20 1.34	1.30	1.30* 1.20* 1.30*	1.27*	Scott-Sanchis
8	0.86 0.87 0.85	0.86	0.92 0.92 0.87	0.90	Scott-Sanchis
9	1.05 1.05 1.05	1.05	1.05 1.05 1.05	1.05	Scott-Sanchis
10	1.02 1.00 1.00	1.01	1.00 1.00 1.04	1.01	Megregian-Maier
11	0.93 0.89 0.91	0.91	0.90 0.95 0.90	0.92	Scott-Sanchis
12	0.98 1.24 0.99	1.07	1.10 1.06 1.02	1.06	Megregian-Maier
13	1.13 1.11 1.13	1.12	1.20 1.20 1.05	1.15	Lamar

*Second number estimated to be zero

Lab. No.	Replicate Values	Average	Replicate Values	Average	Method
14	0.90		0.90		
	0.88	0.91	0.90	0.90	Scott-Sanchis
	0.96		0.90		
15	0.85		0.89		
	0.87	0.84	0.89	0.89	Scott-Sanchis
	0.79		0.90		
16	0.94		0.96		
	0.92	0.94	0.93	0.94	Megregian-Maier
	0.96		0.94		
17	1.14		1.20*		
	1.09	1.11	1.20*	1.20*	Not Identified
	1.10		1.20*		
18	----		----		
	----	----	----	----	None
	----		----		
19	1.00		0.90*		
	0.98	0.97	0.90*	0.90*	Scott-Sanchis
	0.96		0.90*		
	0.92				
20	1.20		0.65		
	1.24	1.23	1.05	0.78	Megregian-Maier
	1.26		0.65		
21	1.00		0.64		
	0.89	0.93	0.66	0.63	Megregian-Maier
	0.89		0.60		
22	0.94		1.21		
	0.99	0.97	1.14	1.18	Thorium Nitrate
	0.98		1.14		
23	1.00		0.90		
	1.10	1.03	1.00	0.95	Scott-Sanchis
	1.00		0.95		
24	----		----		
	----	----	----	----	None
	----		----		
25	1.02		----		
	0.98	1.00	----	----	None
	1.01		----		
26	1.00*		1.00*		
	1.00*	1.03	1.00*	0.93	Scott-Sanchis
	1.08		0.80		
27	1.00		----		
	1.00	0.98	----	----	None
	0.94		----		
SEC	0.96		0.92		
	0.96	0.95	0.88	0.91	Megregian-Maier
	0.94		0.94		

*Second number estimated to be zero

COMPARISON OF REPLICATE VALUES
SOLUTION B - 0.76 mg/l FLUORIDE
NON DISTILLED

Lab. No.	ECR METHOD Replicate Values	ECR METHOD Average	OTHER METHODS Replicate Values	OTHER METHODS Average	OTHER METHODS Method
1	0.61		0.55		
	0.59	0.58	0.55	0.55	Megregian-Maier
	0.55		0.55		
2	0.79		0.60		
	0.79	0.79	0.60	0.60	Scott-Sanchis
	0.78		0.60		
3	0.60		0.60		
	0.63	0.61	0.60	0.60	Scott-Sanchis
	0.59		0.60		
4	0.48		0.87		
	0.93	0.63	0.72	0.67	Megregian-Maier
	0.48		0.47		
5	0.65		0.54		
	0.64	0.63	0.58	0.58	Megregian-Maier
	0.60		0.60		
6	0.63		0.65		
	0.63	0.62	0.65	0.65	Scott-Sanchis
	0.60		0.65		
7	0.80		0.60*		
	0.78	0.79	0.60*	0.60*	Scott-Sanchis
	0.80		0.60*		
8	0.65		0.63		
	0.75	0.72	0.63	0.63	Scott-Sanchis
	0.76		0.63		
9	1.13		0.75		
	1.14	1.14	0.60	0.70	Scott-Sanchis
	1.15		0.75		
10	0.27		0.52		
	0.24	0.25	0.50	0.51	Megregian-Maier
	0.25		0.50		
11	0.59		0.60		
	0.58	0.59	0.60	0.60	Scott-Sanchis
	0.62		0.60		
12	0.57		0.64		
	0.57	0.58	0.58	0.61	Megregian-Maier
	0.61		0.60		
13	0.12		0.60		
	0.16	0.14	0.50	0.50	Lamar
	0.13		0.40		

*Second number estimated to be zero

Lab. No.	Replicate Values	Average	Replicate Values	Average	Method
14	0.76		0.61		
	0.82	0.79	0.62	0.61	Scott-Sanchis
	0.80		0.61		
15	0.71		0.80		
	0.62	0.67	0.80	0.80	Scott-Sanchis
	0.68		0.79		
16	0.66		0.57		
	0.67	0.67	0.62	0.61	Megregian-Maier
	0.67		0.63		
17	0.45		0.60*		
	0.54	0.50	0.60*	0.60*	Not Identified
	0.50		0.60*		
18	0.34		0.48		
	0.33	0.33	0.48	0.48	Megregian-Maier
	0.33		0.48		
19	0.82		0.60*		
	0.65	0.71	0.60*	0.60*	Scott-Sanchis
	0.66		0.60*		
	0.70				
20	0.66		0.00*		
	0.82	0.72	0.00*	0.00*	Megregian-Maier
	0.69		0.00*		
21	0.60		0.72		
	0.61	0.60	0.69	0.67	Megregian-Maier
	0.60		0.60		
22	1.03		1.71		
	1.03	1.03	1.64	1.67	Thorium Nitrate
	1.04		1.65		
23	0.78		0.55		
	0.78	0.78	0.55	0.58	Scott-Sanchis
	0.78		0.60		
24	0.64		0.70		
	0.57	0.60	0.68	0.68	Modified ECR
	----		0.65		
25	0.88		----		
	0.90	0.90	----	----	None
	0.92		----		
26	0.90		0.55		
	0.90	0.87	0.55	0.54	Scott-Sanchis
	0.80		0.52		
27	0.74		----		
	0.64	0.71	----	----	None
	0.74		----		
SEC	0.77		0.51		
	0.79	0.78	0.47	0.50	Megregian-Maier
	0.79		0.51		

*Second number estimated to be zero

COMPARISON OF REPLICATE VALUES
SOLUTION B - 0.76 mg/1 FLUORIDE
DISTILLED

Lab. No.	ECR METHOD		OTHER METHODS		
	Replicate Values	Average	Replicate Values	Average	Method
1	0.72 0.69 0.73	0.71	0.72 0.66 0.63	0.67	Megregian-Maier
2	0.73 0.78 0.73	0.75	0.78 0.78 0.78	0.78	Scott-Sanchis
3	0.70 0.62 0.65	0.66	0.60 0.60 0.60	0.60	Scott-Sanchis
4	0.48 1.86 0.48	0.94	1.02 0.72 0.00	0.58	Megregian-Maier
5	0.76 0.76 0.76	0.76	0.72 0.73 0.81	0.76	Megregian-Maier
6	0.71 0.71 0.72	0.71	0.75 0.75 0.75	0.75	Scott-Sanchis
7	1.38 1.30 1.16	1.28	1.30* 1.10* 1.00*	1.13	Scott-Sanchis
8	0.74 0.75 0.76	0.75	0.78 0.78 0.78	0.78	Scott-Sanchis
9	0.60 0.60 0.60	0.60	0.60 0.60 0.60	0.60	Scott-Sanchis
10	0.84 0.82 0.80	0.82	0.76 0.80 0.84	0.80	Megregian-Maier
11	0.73 0.77 0.75	0.75	0.70 0.75 0.75	0.73	Scott-Sanchis
12	1.12 1.02 1.14	1.09	1.00 1.10 0.91	1.00	Megregian-Maier
13	0.87 0.87 0.96	0.90	0.45 0.45 0.45	0.45	Lamar

*Second number estimated to be zero

Lab. No.	Replicate Values	Average	Replicate Values	Average	Method
14	0.73		0.80		
	0.77	0.78	0.80	0.80	Scott-Sanchis
	0.84		0.80		
15	0.71		0.81		
	0.78	0.78	0.78	0.79	Scott-Sanchis
	0.85		0.78		
16	0.84		0.84		
	0.86	0.85	0.86	0.86	Megregian-Maier
	0.84		0.88		
17	0.79		0.80*		
	0.79	0.81	0.80*	0.80*	Not Identified
	0.84		0.80*		
18	----		----		
	----	----	----	----	None
	----		----		
19	0.78		0.70*		
	0.80	0.82	0.70*	0.70	Scott-Sanchis
	0.86		0.70*		
	0.82				
20	1.12		0.74		
	1.09	1.10	1.15	0.96	Megregian-Maier
	1.09		1.00		
21	0.39		0.40		
	0.40	0.48	0.50	0.50	Megregian-Maier
	0.65		0.60		
22	0.97		0.97		
	0.93	0.95	0.97	0.95	Thorium Nitrate
	0.94		0.91		
23	1.18		0.90		
	1.22	1.15	1.00	0.90	Scott-Sanchis
	1.06		0.80		
24	----		----		
	----	----	----	----	None
	----		----		
25	0.89		----		
	0.89	0.88	----	----	None
	0.87		----		
26	0.80		0.70		
	0.88	0.81	0.75	0.72	Scott-Sanchis
	0.75		0.70		
27	0.94		----		
	0.98	0.95	----	----	None
	0.94		----		
SEC	0.72		0.76		
	0.80	0.77	0.94	0.83	Megregian-Maier
	0.80		0.80		

*Second number estimated to be zero

COMPARISON OF REPLICATE VALUES
SOLUTION C - 0.87 mg/l FLUORIDE
NON DISTILLED

Lab. No.	ECR METHOD Replicate Values	ECR METHOD Average	OTHER METHODS Replicate Values	OTHER METHODS Average	OTHER METHODS Method
1	0.98		1.19		
	1.01	0.98	1.26	1.24	Megregian-Maier
	0.94		1.27		
2	1.03		0.90		
	1.07	1.06	0.90	0.90	Scott-Sanchis
	1.07		0.90		
3	1.01		0.90		
	1.01	1.01	0.90	0.90	Scott-Sanchis
	1.02		0.90		
4	0.93		1.14		
	0.93	0.93	1.29	1.18	Megregian-Maier
	0.93		1.12		
5	1.06		1.26		
	1.08	1.07	1.37	1.30	Megregian-Maier
	1.08		1.30		
6	1.00		1.12		
	1.02	1.01	1.12	1.12	Scott-Sanchis
	1.02		1.12		
7	1.18		0.90*		
	1.18	1.18	0.90*	0.90*	Scott-Sanchis
	1.18		0.90*		
8	1.00		0.83		
	1.04	0.99	0.82	0.81	Scott-Sanchis
	0.94		0.78		
9	1.04		1.05		
	1.04	1.04	1.05	1.05	Scott-Sanchis
	1.04		1.05		
10	0.99		1.00		
	0.96	0.98	1.00	0.99	Megregian-Maier
	0.98		0.98		
11	0.82		0.90		
	0.87	0.85	0.90	0.90	Scott-Sanchis
	0.86		0.90		
12	1.00		1.27		
	1.12	1.08	1.32	1.30	Megregian-Maier
	1.12		1.32		
13	0.99		0.65		
	1.00	1.00	0.75	0.68	Lamar
	1.00		0.65		

*Second number estimated to be zero

Lab. No.	Replicate Values	Average	Replicate Values	Average	Method
14	1.24		0.91		
	1.20	1.22	0.92	0.91	Scott-Sanchis
	1.22		0.92		
15	1.05		0.92		
	1.07	1.06	0.91	0.92	Soctt-Sanchis
	1.07		0.92		
16	0.96		1.21		
	0.98	0.98	1.22	1.23	Megregian-Maier
	0.99		1.27		
17	0.83		1.00*		
	0.83	0.84	1.00*	1.00*	Not Identified
	0.85		1.00*		
18	1.06		1.22		
	1.08	1.07	1.22	1.22	Megregian-Maier
	1.08		1.22		
19	0.88		0.70*		
	0.96	0.99	0.70*	0.70*	Scott-Sanchis
	1.04		0.70*		
	1.01				
20	1.37		0.85		
	1.45	1.42	0.85	0.97	Megregian-Maier
	1.43		1.20		
21	1.05		1.27		
	0.98	1.00	1.23	1.20	Megregian-Maier
	0.98		1.10		
22	0.99		1.66		
	0.99	0.99	1.65	1.67	Thorium Nitrate
	0.99		1.69		
23	0.77		0.70		
	0.86	0.80	0.70	0.70	Scott-Sanchis
	0.77		0.70		
24	1.04		0.98		
	0.99	1.01	0.98	1.00	Modified ECR
	----		1.05		
25	0.96		----		
	1.02	1.00	----	----	None
	1.02		----		
26	1.14		0.85		
	1.14	1.14	0.80	0.83	Scott-Sanchis
	1.16		0.85		
27	0.94		----		
	0.84	0.91	----	----	None
	0.94		----		
SEC	1.22		1.31		
	1.26	1.24	1.33	1.31	Megregian-Maier
	1.25		1.30		

*Second number estimated to be zero

COMPARISON OF REPLICATE VALUES
SOLUTION C - 0.87 mg/1 FLUORIDE
DISTILLED

Lab. No.	ECR METHOD Replicate Values	ECR METHOD Average	OTHER METHODS Replicate Values	OTHER METHODS Average	OTHER METHODS Method
1	1.05		1.11		
	0.93	1.01	1.23	1.05	Megregian-Maier
	1.05		0.81		
2	0.95		1.00		
	1.05	1.00	1.00	1.00	Scott-Sanchis
	1.00		1.00		
3	0.93		1.00		
	0.93	0.93	1.05	1.02	Scott-Sanchis
	0.94		1.00		
4	1.41		1.14		
	0.93	0.94	1.14	1.13	Megregian-Maier
	0.48		1.12		
5	0.95		1.00		
	0.96	0.96	0.94	1.00	Megregian-Maier
	0.97		1.05		
6	0.80		0.83		
	0.80	0.80	0.83	0.83	Scott-Sanchis
	0.80		0.83		
7	1.22		1.10*		
	0.94	1.03	0.90*	0.97	Scott-Sanchis
	0.92		0.90*		
8	0.85		0.86		
	0.86	0.86	0.83	0.84	Scott-Sanchis
	0.86		0.83		
9	1.08		1.05		
	1.04	1.04	0.90	0.99	Scott-Sanchis
	1.02		1.05		
10	1.00		0.88		
	0.98	0.98	1.00	0.95	Megregian-Maier
	0.96		0.96		
11	0.87		0.85		
	0.89	0.88	0.85	0.85	Scott-Sanchis
	0.88		0.85		
12	0.68		1.00		
	0.60	0.64	1.00	1.01	Megregian-Maier
	0.63		1.02		
13	1.05		1.05		
	1.02	1.03	1.05	1.05	Lamar
	1.02		1.05		

*Second number estimated to be zero

Lab. No.	Replicate Values	Average	Replicate Values	Average	Method
14	0.92		0.90		
	0.91	0.91	0.90	0.87	Scott-Sanchis
	0.90		0.80		
15	0.79		0.88		
	0.78	0.79	0.87	0.88	Scott-Sanchis
	0.80		0.89		
16	0.98		0.95		
	0.97	0.97	0.94	0.95	Megregian-Maier
	0.97		0.97		
17	0.74		0.80*		
	0.67	0.71	0.80*	0.80*	Not Identified
	0.72		0.80*		
18	----		----		
	----	----	----	----	None
	----		----		
19	0.96		0.90*		
	1.00	0.97	0.90*	0.90*	Scott-Sanchis
	0.96		0.90*		
20	1.32		1.15		
	1.40	1.37	1.32	1.22	Megregian-Maier
	1.39		1.20		
21	1.21		1.00		
	1.21	1.21	1.00	1.05	Megregian-Maier
	1.21		1.10		
22	0.95		1.25		
	0.93	0.94	1.32	1.24	Thorium Nitrite
	0.93		1.14		
23	1.28		1.00		
	1.14	1.11	1.00	0.97	Scott-Sanchis
	0.92		0.90		
24	----		----		
	----	----	----	----	None
	----		----		
25	0.99		----		
	0.96	0.97	----	----	None
	0.97		----		
26	0.86		0.90		
	1.14	0.95	1.10	0.93	Scott-Sanchis
	0.86		0.80		
27	0.97		----		
	1.02	1.00	----	----	None
	1.00		----		
SEC	0.84		0.84		
	0.88	0.87	0.80	0.85	Megregian-Maier
	0.90		0.92		

*Second number estimated to be zero

SUMMARY OF ARITHMETIC MEANS

SAMPLE III

Lab. No.	SOLUTION A - 0.92 mg/l				SOLUTION B - 0.76 mg/l				SOLUTION C - 0.87 mg/l			
	ECR		COMPARATIVE		ECR		COMPARATIVE		ECR		COMPARATIVE	
	DIST.	NON DIST.	DIST.	NON DIST.	DIST.	NON DIST.	DIST.	NON DIST.	DIST.	NON DIST.	DIST.	NON DIST.
SEC	0.95	0.96	0.91	0.91	0.77	0.78	0.83	0.50	0.87	1.24	0.85	1.31
1	0.92	0.91	0.90	0.92	0.71	0.58	0.67	0.55	1.01	0.98	1.05	1.24
2	0.84	0.91	0.88	0.95	0.75	0.79	0.78	0.60	1.00	1.06	1.00	0.90
3	0.85	0.85	0.79	0.93	0.66	0.61	0.60	0.60	0.93	1.01	1.02	0.90
4	1.70	1.09	1.86	1.01	0.94	0.63	0.58	0.67	0.94	0.93	1.13	1.18
5	0.99	0.96	0.93	0.97	0.76	0.63	0.76	0.58	0.96	1.07	1.00	1.30
6	0.92	0.91	0.95	0.95	0.71	0.62	0.75	0.65	0.80	1.01	0.83	1.12
7	1.30	0.88	1.27	0.90	1.28	0.79	1.13	0.60	1.03	1.18	0.97	0.90
8	0.86	0.93	0.90	0.93	0.75	0.72	0.78	0.63	0.86	0.99	0.84	0.81
8A	----	----	0.82	0.92	----	----	0.72	0.82	----	----	0.81	1.01
9	1.05	1.01	1.05	1.00	0.60	1.14	0.60	0.70	1.04	1.04	0.99	1.05
10	1.01	0.94	1.01	1.00	0.82	0.25	0.80	0.51	0.98	0.98	0.95	0.99

11	0.91	0.89	0.92	0.90	0.75	0.59	0.73	0.60	0.88	0.85	0.85	0.90
12	1.07	1.06	1.06	1.00	1.09	0.58	1.00	0.61	0.64	1.08	1.01	1.30
13	1.12	0.90	1.15	0.95	0.90	0.14	0.45	0.50	1.03	1.00	1.05	0.68
14	0.91	0.98	0.90	0.92	0.78	0.79	0.80	0.61	0.91	1.22	0.87	0.91
15	0.84	0.84	0.89	0.90	0.78	0.67	0.79	0.80	0.79	1.06	0.88	0.92
16	0.94	0.95	0.94	0.95	0.85	0.67	0.86	0.61	0.97	0.98	0.95	1.23
17	1.11	0.80	1.20	0.80	0.81	0.50	0.80	0.60	0.71	0.84	0.80	1.00
18	----	0.95	----	0.96	----	0.33	----	0.48	----	1.07	----	1.22
19	0.97	0.93	0.90	0.90	0.82	0.71	0.70	0.60	0.97	0.99	0.90	0.70
20	1.23	1.17	0.78	0.13	1.10	0.72	0.96	0.00	1.37	1.42	1.22	0.97
21	0.93	0.89	0.63	0.91	0.48	0.60	0.50	0.67	1.21	1.00	1.05	1.20
22	0.97	1.04	1.18	1.08	0.95	1.03	0.95	1.67	0.94	0.99	1.24	1.67
23	1.03	0.92	0.95	0.93	1.15	0.78	0.90	0.58	1.11	0.80	0.97	0.70
24	----	0.94	----	0.93	----	0.60	----	0.68	----	1.01	----	1.00
25	1.00	0.98	----	----	0.88	0.90	----	----	0.97	1.00	----	----
26	1.03	0.98	0.93	0.92	0.81	0.87	0.72	0.54	0.95	1.14	0.93	0.83
27	0.98	0.99	----	----	0.95	0.71	----	----	1.00	0.91	----	----

COMMENTS ON DISTILLATION PROCEDURES

Lab. 1 — The rate of the distillation and the temperature have to be watched closely. Even when this is done, the results on a sample may vary considerably.
ST. METH., 10th ed.

Lab. 2 — Method is time-consuming. There is some disagreement among various investigators regarding the best temperature at which to carry out the distillation.
MODIFIED WILLARD AND WINTER

Lab. 3 — High sulfate corrections were required for the ECR Method; not true of the Scott-Sanchis Method which tolerates a high concentration of sulfate.
ST. METH., 10th ed.

Lab. 4 — Very careful procedure must be obtained to avoid loss of fluoride, improvised distillation apparatus is not sufficient.
ST. METH., 10th ed., MODIFIED

Lab. 5 — None.
ST. METH., 10th ed.

Lab. 6 — No further remarks.
ST. METH., 10th ed.

Lab. 7 — Gives high results even with careful temperature control. Obviates any advantage gained by supposedly eliminating interfering substances. Exceedingly high results if temperature exceeds 150° C. Sulfuric acid is distilled over in distillate.
ST. METH., 10th ed.

Lab. 8 — The distillation procedure requires considerable time and constant attention.
ST. METH., 10th ed.

Lab. 9 — None.
PERCHLORIC ACID WITH STEAM

Lab. 10 — First distillates were distilled at prescribed rate and temperature of 140° ± 2°. These distillates gave highly erratic results as listed below. Speculation and examination revealed a considerable

amount of sulfate coming over in the distillate. Distilling at a slower rate and never exceeding 135° C finally gave sulfate free distillates. They were used in the final tabulations. Results from the first distillates gave the following answers using the ECR method:

Sample A	Sample B	Sample C
2.86	1.82	2.52
2.14	1.90	2.12
2.28	2.28	2.16
4.20	.88	2.12
2.02	.73	2.16
1.62	.88	1.26

MODIFIED WILLARD AND WINTER

Lab. 11 No difficulty if rate of distillation and temperature are held to levels prescribed by method.

WILLARD AND WINTER WITH PERCHLORIC ACID

Lab. 12 Very time-consuming and exacting. Sulfate carried over if temperature is allowed to exceed 150° for only a few seconds. ST. METH., 10th ed.

Lab. 13 No difficulty except some bumping, especially on Sample B. ST. METH., 10th ed.

Lab. 14 This method simplifies distillation by using only one burner for heating. No sulfates are distilled over and no corrections necessary. For most of our routine work, it is not necessary to make distillations which are made only when interferences are apparent. Distillation recovers about 95 - 97% for us. ST. METH., 10th ed.

Lab. 15 Too time-consuming for routine work. ST. METH., 10th ed.

Lab. 16 Unsatisfactory - dilution increases possibility of error, and sulfate carryover must be checked. ST. METH., 10th ed.

Lab. 17 Sufficient sample was distilled so that the six aliquots could be obtained from the single distillation. ST. METH., 10th ed.

Lab. 18 Difficulty encountered with distillation process. Excessive sulfate carried over with distillate. ST. METH., 10th ed.

Lab. 19 The main difficulty in the distillation procedure was in adjusting the flow of distilled water so as to maintain a temperature range of 138 - 145° C. Constant attendance was necessary to keep the temperature within the prescribed range. ST. METH., 10th ed.

Lab. 20 Very rapid - temperature must be watched at all times.
FRAZIER AND OLDFIELD

Lab. 21 The temperature is very hard to keep at 140 - 150°. Quite a bit of the distillate comes over at 110. Would this affect the results?
ST. METH., 10th ed.

Lab. 22 When the distillation procedure is carried out correctly the removal of interfering substances is adequately obtained. This distillation is time-consuming and requires constant control of temperatures. It is doubtful that greater than 95% yield can be obtained. WILLARD AND WINTER WITH PERCHLORIC ACID

Lab. 23 Satisfactory for use with Scott-Sanchis Method. Temperature control requires constant attention of staff member. We feel that if ECR method is to be used on distilled samples, the possibility of sulfate coming over during distillation should not be overlooked.

A short study done by this lab shows the following:

Temperature of Distillation	Sulfate Concentration in Distillate
120° C	7.4 mg/l
130° C	61 mg/l
140° C	135 mg/l
150° C	136 mg/l

Distillation flask contained 50 ml distilled water and 15 ml conc. H_2SO_4. 150 ml distillate collected by steam distillation according to 10th edition, Standard Methods. ST. METH., 10th ed.

Lab. 24	None.	NO DISTILLATION
Lab. 25	None.	ST. METH., 10th ed.
Lab. 26	Precautions necessary to prevent SO_4 carry over especially when ECR method is being used. Moisture trap ahead of condenser helpful.	ST. METH., 10th ed.
Lab. 27	None.	NO DISTILLATION

SUMMARY OF COMMENTS CONCERNING THE DISTILLATION PROCEDURES

Twenty-one participants furnished comments on the distillation procedures. A summary of these comments is as follows:

(1) The distillation procedure requires constant attention for good temperature control and is time-consuming.

(2) The hazard from sulfate carry over is difficult to control.

Laboratory #23 reported a sulfate concentration in the distillate ranging from 7.4 to 136 mg/1 when the temperature varied from 120° C to 150° C. It is suggested that a pH measurement of the distillate may be used as a criterion of acid carry over and indirectly a measure of sulfate in the distilled sample.

REFERENCE

PROBLEMS IN ESTIMATING FLUORIDES IN WATER, Kramer, H. P., Kroner, R. C. and Ballinger, D. G., JAWWA, 48:573, (May, 1956).

COMMENTS CONCERNING THE ECR METHOD

Lab. 1 The rapidity and the stability of this method are very advantageous. The readings seem to vary during the first five or ten minutes but after fifteen minutes they remain constant. The difference between the five-minute reading and the twenty-minute reading is only 0.4 mg per liter of fluoride.

Lab. 2 Very satisfactory for low mineral waters.

Lab. 3 Strong point in favor of this method is the saving of time. If sulfate could be complexed or removed prior to color development, method would be greatly improved.

Lab. 4 Appears to give equal results, but from this work it has no advantage in routine analysis. The range of adsorption seems to be too small.

Lab. 5 None.

Lab. 6 The undistilled samples were analyzed (in the case of the B and C solutions) by PROCEDURE 4.3 of instructions sent with the samples. All other determinations were made according to PROCEDURE 4.2. Corrections for sulfates were made on the non-distilled samples using the NOMOGRAPH.

The time may have been slightly less than ½ hour at which the standards became permanently consistent. Eleven tubes were used in making the standard curve. Each tube was treated with ECR; then each tube was treated with the zirconyl-acid in the same order. After all tubes were treated and thoroughly mixed, they seemed to be permanently stabilized a few minutes. If corrections can be made, as it appears they can, it seems that this method has many advantages over some of the other methods. My experience with this method has been too brief for me to form any definite and final opinion.

Lab. 7 Appears to give more consistent results than distillation procedure, plus Scott-Sanchis Method. Much less tedious and more reliable than distillation procedure. For water of unknown chemical composition interferences would compensate without chemical analysis or distillation. ECR method would be ideal for fluoride control work, also could be used by water operators, possibly with B and L Spectronic 20.

Lab. 8 The method seems to be quite simple and rapid when compared to the method presently being used in this laboratory.

Lab. 9 The method seems to be capable of quite good results. However, it appears to be sensitive to small changes in procedure and the scale spread is rather narrow giving a flat curve if plotted directly in ppm. We had some difficulity in duplicating results from day to day on the raw water samples 3B and 3C. However, the agreement was good on duplicate sample on any one day. I believe it would be necessary for each laboratory to establish their own best conditions and technic before adopting the ECR method.

Lab. 10 Until our discovery that our distillates carried varying amounts of sulfate, our results were not in harmony, and no reliance could be placed in the answers..

The standards used to check the standard curve from day to day also had a tendency to deviate from the original readings although a slight variation in temperature may have been partly responsible.

The method is extremely sensitive to the presence of sulfates, and unless some compensation is made for them, the results were unreliable. For single determinations, the method may present some saving of time, but for a large number of samples, the method we employ has definite advantages.

The high concentration of acid in the zirconium reagent, presents some hazard, and in running a large number of samples may become a rather disagreeable project.

Lab. 11 For routine work we prefer a procedure which may be evaluated visually. This method cannot. Also, the sulfate error is considerable and in a laboratory such as ours, which receives samples from as many as 1200 different water supplies, a tremendous amount of extra work would be required to determine sulfates for corrective purposes.

Lab. 12 The only advantage that I see in this method is the shorter reaction time.

Lab. 13 This method seems to be a great improvement over the present standard methods, especially on the distilled samples. Considerable difficulty in securing checks on Sample B was experienced.

Results reported on that sample are the three closest of nine tests. The important advantages of this method are the color stability and immediate reading of samples, eliminating the time element involved in the other methods.

Lab. 14 On blanks your ECR reagent gave an optical density of .566-.575 with variations up to .598-.610.

"Harleco ECR for biological staining" gave optical density blanks much like those in reprint of .875-.900.

Sulfate correction does not appear to make for simplicity and quickness. We found that samples that are distilled should be compared with a curve made from distilled standards.

Lab. 15 Seems difficult to incorporate in daily laboratory work.

Lab. 16 Excellent for distillates if sulfate is kept low. For undistilled samples, sulfate correction is hazardous and annoying.

Lab. 17 Chloride, sulfate, aluminum, iron, and alkalinity were determined on the samples and corrections made where necessary. Sample III B was corrected for aluminum.

The ECR method appears to be less time-consuming than the Zirconium-Alizarin method.

Lab. 18 None.

Lab. 19 The procedure for setting up the test was simple and straightforward, and did not require too much time to perform. However, the color developed by the standards was not immediate and stable as stated in the reference. The color read immediately and after one hour showed higher optical density than when read two to four hours later. The curves developed from the standards when read immediately were erratic and did not form a straight line. It was only when read after two hours standing that a fairly straight line was obtained.

The final results obtained by this method all agreed within .08 mg/l with the exception of two results. The exceptions were the results obtained from the undistilled portions of samples B and C in which ECR and zirconyl acid solution were added in succession and read after two hours.

In regard to the sulfate nomograph it is stated "multiply by aliquot factor" after making correction for sulfate. However, the nomograph gives all results in ppm. Could the nomograph be in error, or are the instructions in the use of nomograph in error?

Lab. 20 Very satisfactory if sulfates are determined along with analysis.

Lab. 21 It is a very rapid method. I did find though that if the samples were allowed to stand longer than one-half hour after the addition of the reagents, the reading had changed.

Lab. 22 It appears to be a more rapid method for fluoride analysis than the currently most common Scott-Sanchis Method, chiefly in a shorter waiting period. It was noted during analyses of these samples that the time element is critical in ranges above 0.8 ppm of fluoride. In preparing reagent B this lab had trouble in obtaining Zirconyl chloride octalhydrate which would work satisfactorily. It would be of benefit chiefly in Air Pollution Work if this method could be modified so accurate analysis could be performed in the range of 0 to .1 ppm.

Lab. 23 Standard curve has rather steep slope so that small differences in spectrophotometer readings in duplicate samples give rise to large differences in calculated fluoride content.

Procedure is easy to perform.

Sensitivity apparently not improved over Megregian-Maier procedure.

Our experiments show that we are having some SO_4^{--} coming over in the distillate during the F distillation. If this is true with other laboratories, it is a factor to be considered before ECR method is used after distillation. We hope to ascertain if the SO_4^{--} contamination of our distillate is characteristic of our distillation apparatus and/or technique or inherent in the distillation procedure.

Lab. 24 None.

Lab. 25 Voltage interferences from electrical equipment in lab caused variation in absorbence readings on spectrophotometer. A drop in

absorbence was noticed on all samples as time elapsed. The reported results were based on initial readings.

A little difficulty was involved keeping all the samples adjusted to the same temperature.

Lab. 26 Highly sensitive and accurate. Objection seems to be high sulfate correction and necessity of determining the sulfate content.

Lab. 27 The procedure we used is Mr. Thatcher's (USGS) modification of the Megregian ECR procedure. Mr. Thatcher's procedure entitled "Modified Zirconium-Eriochrome Cyanide R. determination of Fluoride and Application to Water" was presented at the September 1956 meeting of the American Chemical Society and is to be published in Analytical Chemistry, .

SUMMARY OF COMMENTS ON ECR METHOD

The summary of the comments regarding the ECR method based on observations of twenty-four laboratories was:

1. The method is simple and rapid.
2. The method is very sensitive to sulfate interference. Nomograph correction not completely satisfactory.
3. The time required for obtaining a stable colored system after addition of all reagents is longer than five minutes.

COMMENTS CONCERNING OTHER METHODS

Lab. 1 The method seems to give satisfactory results on drinking water samples where no interfering substances are present. The disadvantages are that samples with interfering materials have to be distilled and all readings on the spectrophotometer have to be read at exactly one hour.

MEGREGIAN-MAIER 10th ed.

Lab. 2 The method is not easily accurate to two decimal places in milligrams per liter. The second decimal place in the above results is an estimate.

SCOTT-SANCHIS 10th ed.

Lab. 3 This laboratory normally reports fluoride results to the first decimal place. Only occasional routine samples prove difficult due to interference,

SCOTT-SANCHIS 10th ed.

Lab. 4 Seems to give a working accuracy but will vary with temperature and time for color development.

MEGREGIAN-MAIER 10th ed.

Lab. 5 None.

MEGREGIAN-MAIER 10th ed.

Lab. 6 The method seems to have fine possibilities. Three standard curves were made on three different days and they were exactly consistent. For the third curve the unused standards were saved after being treated with both reagents and again read the next day at the same temperature gave exactly the same results as the day before. I have not worked on waters with known interferences. Time has not permitted. Results were not found to be consistent until after ¼ hour.

SCOTT-SANCHIS 10th ed.

Lab. 7 For waters of known chemical composition where interferences are minimal, this is a good routine method. Would not advise

for research work or waters of questionable chemical composition.

SCOTT-SANCHIS 10th ed. WITH HELIGE AQUA TESTER.

Lab. 8 We find the above method tedious but satisfactory from the standpoint of results when the interfering substances are removed or corrected for. On samples containing sulfates and chlorides, equivalent amounts of these ions are added to each of the standards. Alkalinity is neutralized with nitric acid. Color is removed by the use of activated carbon and turbidity removed by filtering. Chlorine is removed by the addition of sodium arsenite or activated carbon. Phosphates interfere seriously.

This method appears to be satisfactory as a screening and routine procedure for untreated waters when sulfate and chloride are known.

SCOTT-SANCHIS 10th ed.

Lab. 9 None. SCOTT-SANCHIS 10th ed.

Lab. 10 Even high concentrations of sulfates which are normally encountered in many of our waters do not interfere with the results. Manipulations are simple, reagents stable and ideal for a large number of routine samples.

MEGREGIAN-MAIER 10th ed. (MODIFIED VISUAL METHOD).

Lab. 11 We have tried all of the proposed methods for fluoride determination and still prefer the Scott-Sanchis method for the reason that we believe that visual color comparisons are more easily made with this method than with any other.

SCOTT-SANCHIS 10th ed.

Lab. 12 Still seems to be the best available.

MEGREGIAN-MAIER 10th ed.

Lab. 13 Difficult to secure good checks on the triplicate tests of the same samples on the non-distilled.

LAMAR 10th ed.

Lab. 14 For our routine work, Scott-Sanchis gives us very good results, visually, generally non-distilled. Distill when it is deemed necessary. Method is simple - not complicated. No sulfate correction

necessary. Same is apparent for phosphates. The only serious interference for us appears to be the aluminum content. This can be removed by adjusting pH to 6.0 to 7.0 and filter off the aluminum hydroxide.

SCOTT-SANCHIS 10th ed.

Lab. 15 The manipulation fits in well with our laboratory routine.

SCOTT-SANCHIS 10th ed.

Lab. 16 Takes too much time.

MEGREGIAN-MAIER 10th ed.

Lab. 17 When corrections are made for bicarbonate, chloride, and sulfate, this method gives satisfactory results in routine work.

ST. METH., 10th ed., MODIFIED

Lab. 18 None. MEGREGIAN-MAIER 10th ed.

Lab. 19 The procedure for this test is relatively simple to set up and do for routine analyses. The precision and accuracy of the test is 0.1 mg F/l.

SCOTT-SANCHIS 10th ed.

Lab. 20 Has proved satisfactory up to this time - with distillation.

MEGREGIAN-MAIER 10th ed.

Lab. 21 I find this method very satisfactory.

MEGREGIAN-MAIER 10th ed.

Lab. 22 It is a satisfactory method for low concentrations (0 to 0.1 ppm) but for high concentrations it requires excessive time to carry out analyses; since samples require dilution for high concentrations it introduces dilution errors.

THORIUM NITRATE TITRATION

Lab. 23 Used routinely in lab. Satisfactory for our needs and liked by most of our chemists.

SCOTT-SANCHIS 10th ed.

Lab. 24 Differs from original procedure in pH, reagent strength, use of reducing agent to eliminate oxidation interference, and use of barium chloride to precipitate sulfate.

ECR, MODIFIED

Lab. 25 NO COMPARISON PERFORMED.

Lab. 26 This method in general use for routine control in water treatment plants. Frequently use permanent type (glass) color disk for standards.

SCOTT-SANCHIS 10th ed.

Lab. 27 None. ECR (THATCHER'S MODIFICATION)

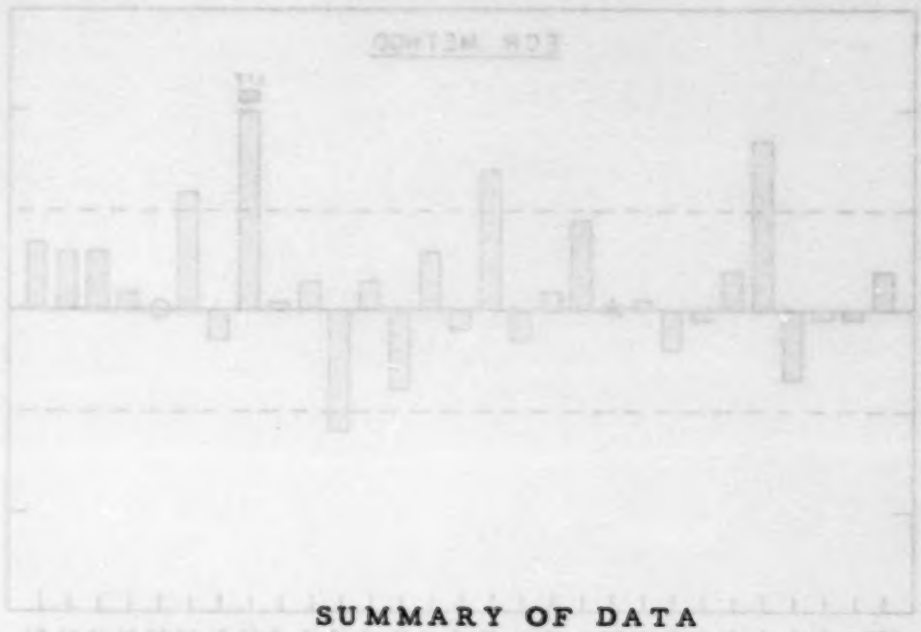
SUMMARY OF COMMENTS ON SCOTT-SANCHIS METHOD

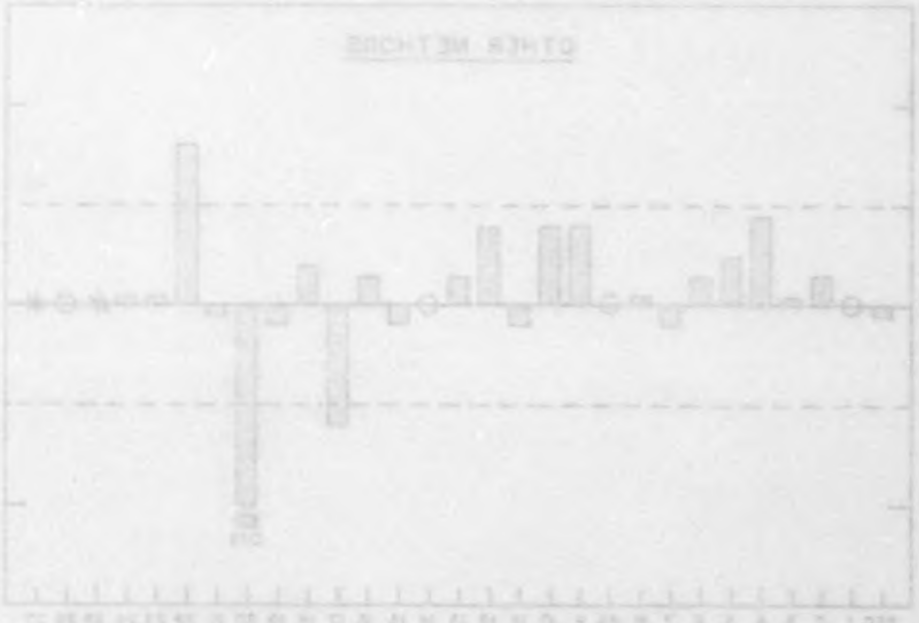
The method is not capable of more than 0.1 mg/l accuracy, but is well suited to routine work. This procedure is apparently preferred because of its simplicity and freedom from interferences.

SUMMARY OF COMMENTS ON MEGREGIAN-MAIER METHOD

Nine laboratories used the Megregian-Maier method and is apparently considered satisfactory by the users. Three groups commented adversely on the time factor involved in this method. In general, the remarks concerning this method do not show any unanimity of opinion.

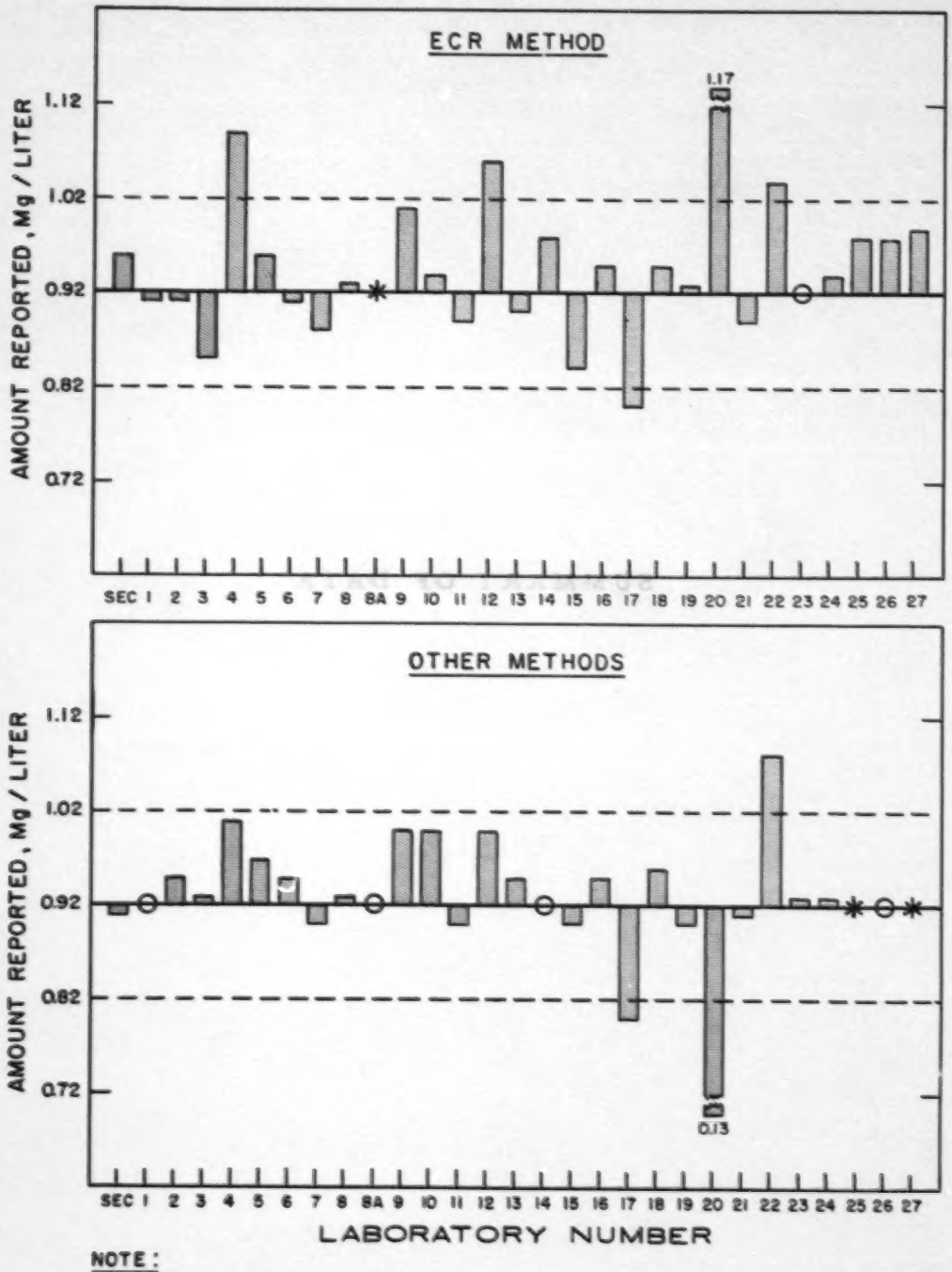
SUMMARY OF DATA





SOLUTION "A"-NON DISTILLED

NO INTERFERENCES



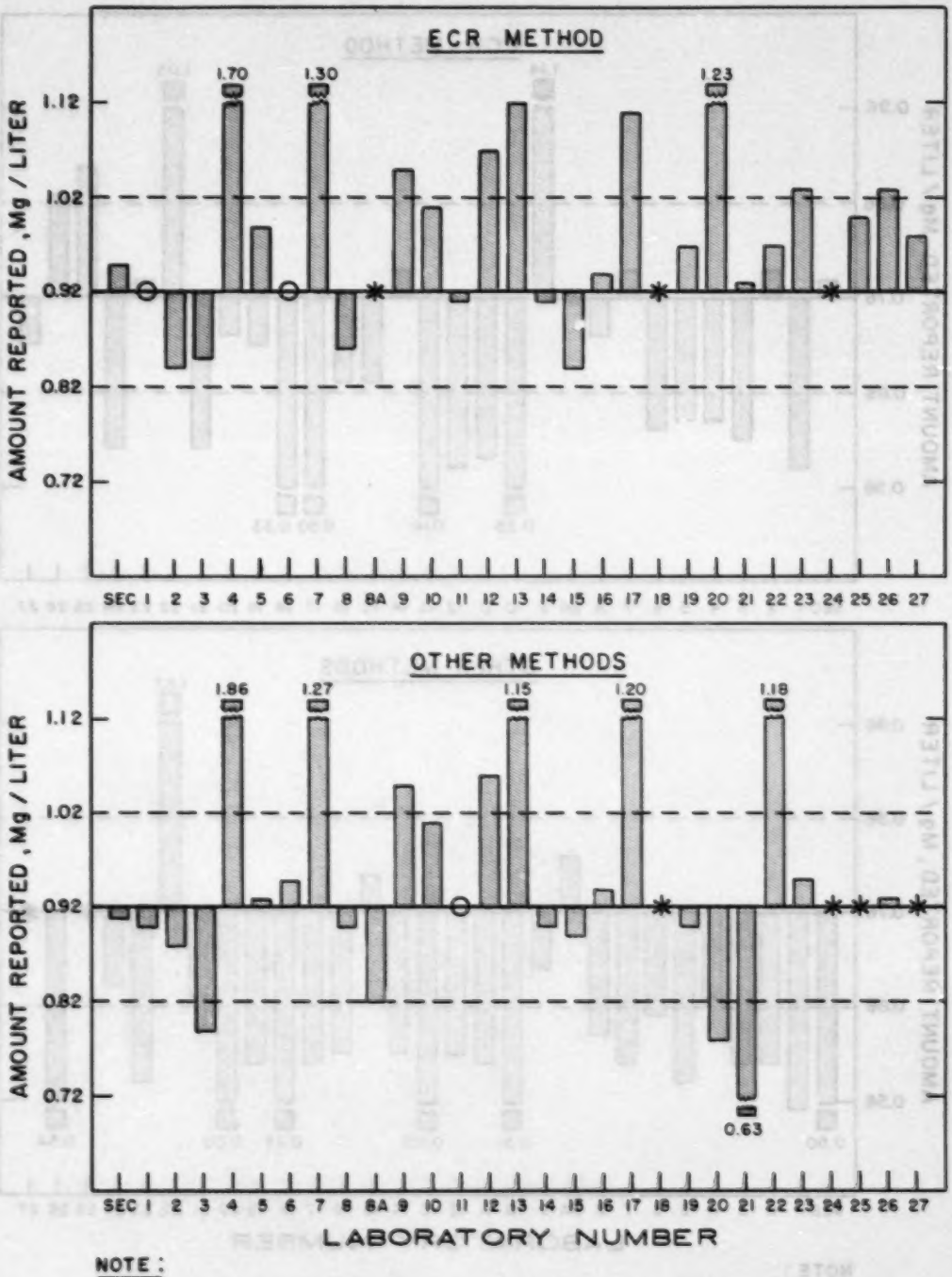
NOTE:

○ = PERFECT RESULTS

✱ = NO ANALYSIS PERFORMED

SOLUTION "A"-DISTILLED

NO INTERFERENCES



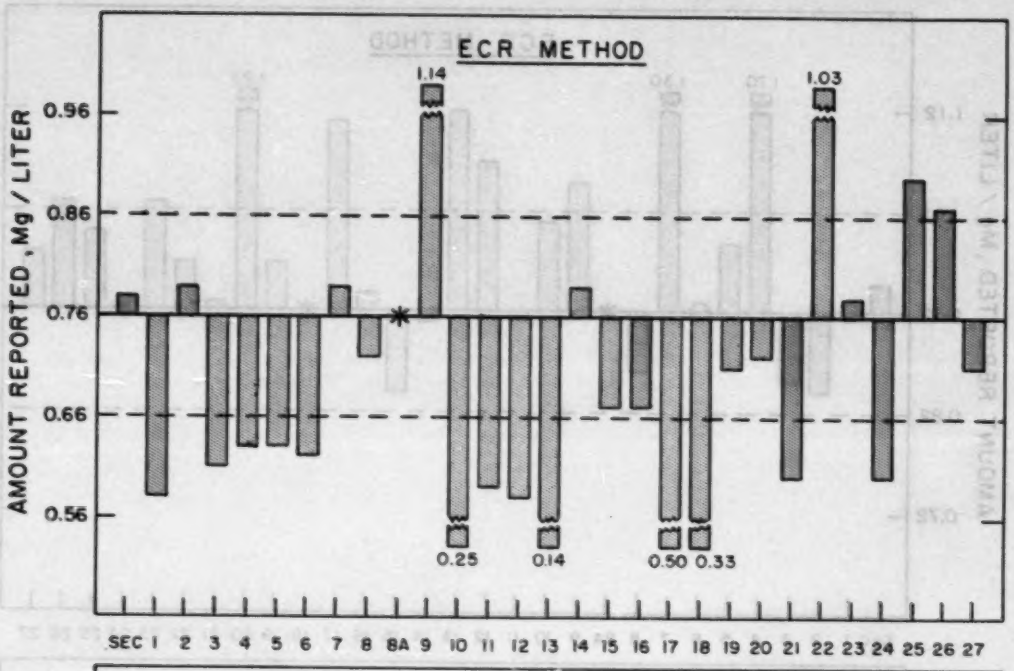
NOTE:

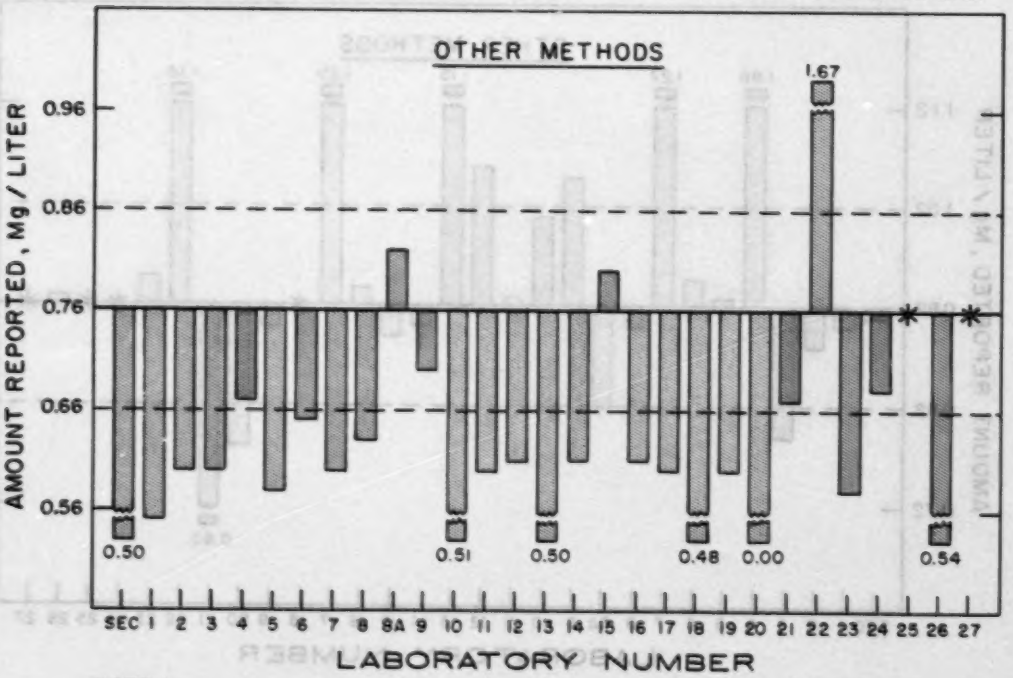
○ = PERFECT RESULTS

✱ = NO ANALYSIS PERFORMED

SOLUTION "B" - NON DISTILLED

CONTAINING 300 MG/L SULFATE, 2.0 MG/L ALUMINUM





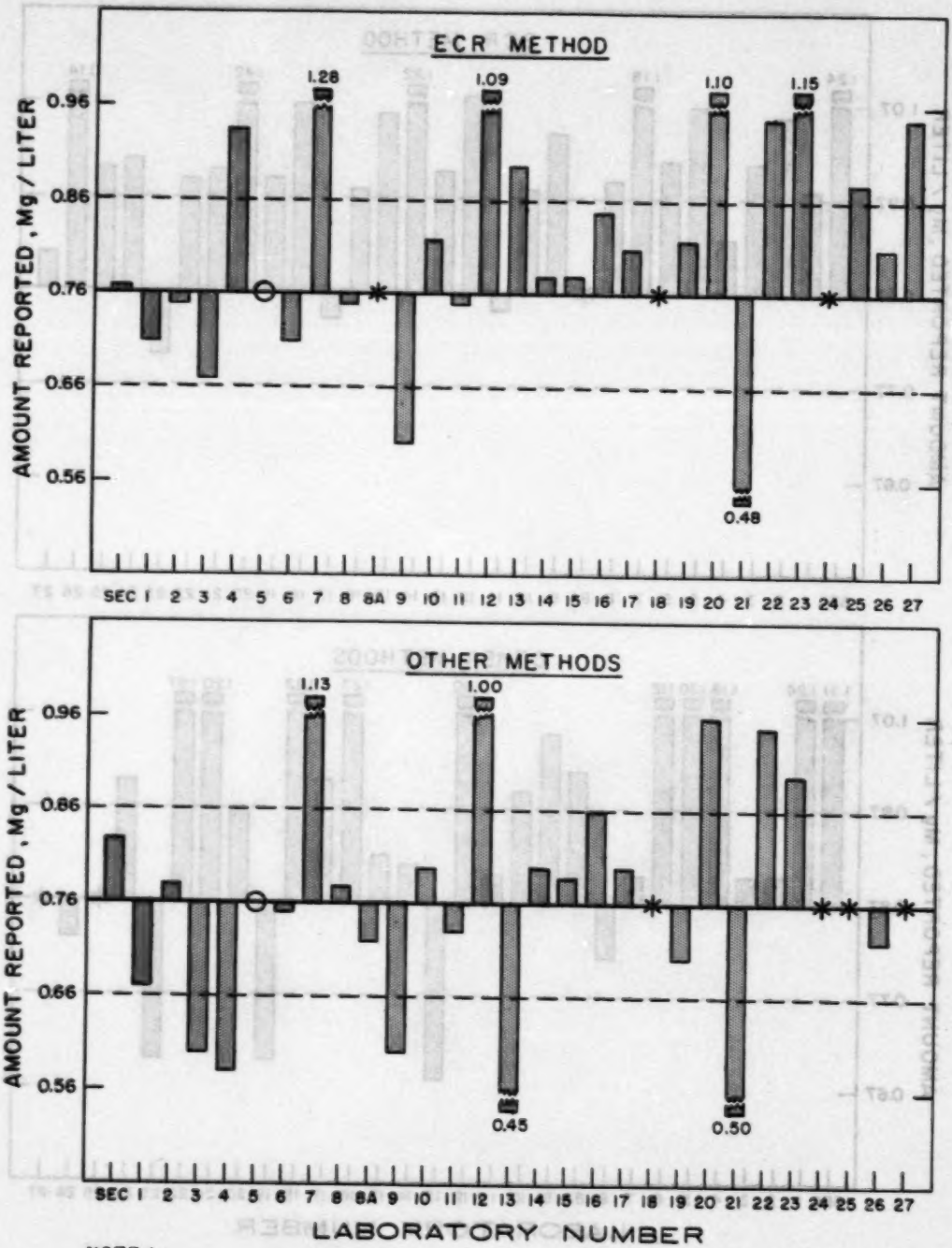
NOTE:

○ = PERFECT RESULTS

✱ = NO ANALYSIS PERFORMED

SOLUTION "B"-DISTILLED

CONTAINING 300 MG/L SULFATE, 2.0 MG/L ALUMINUM



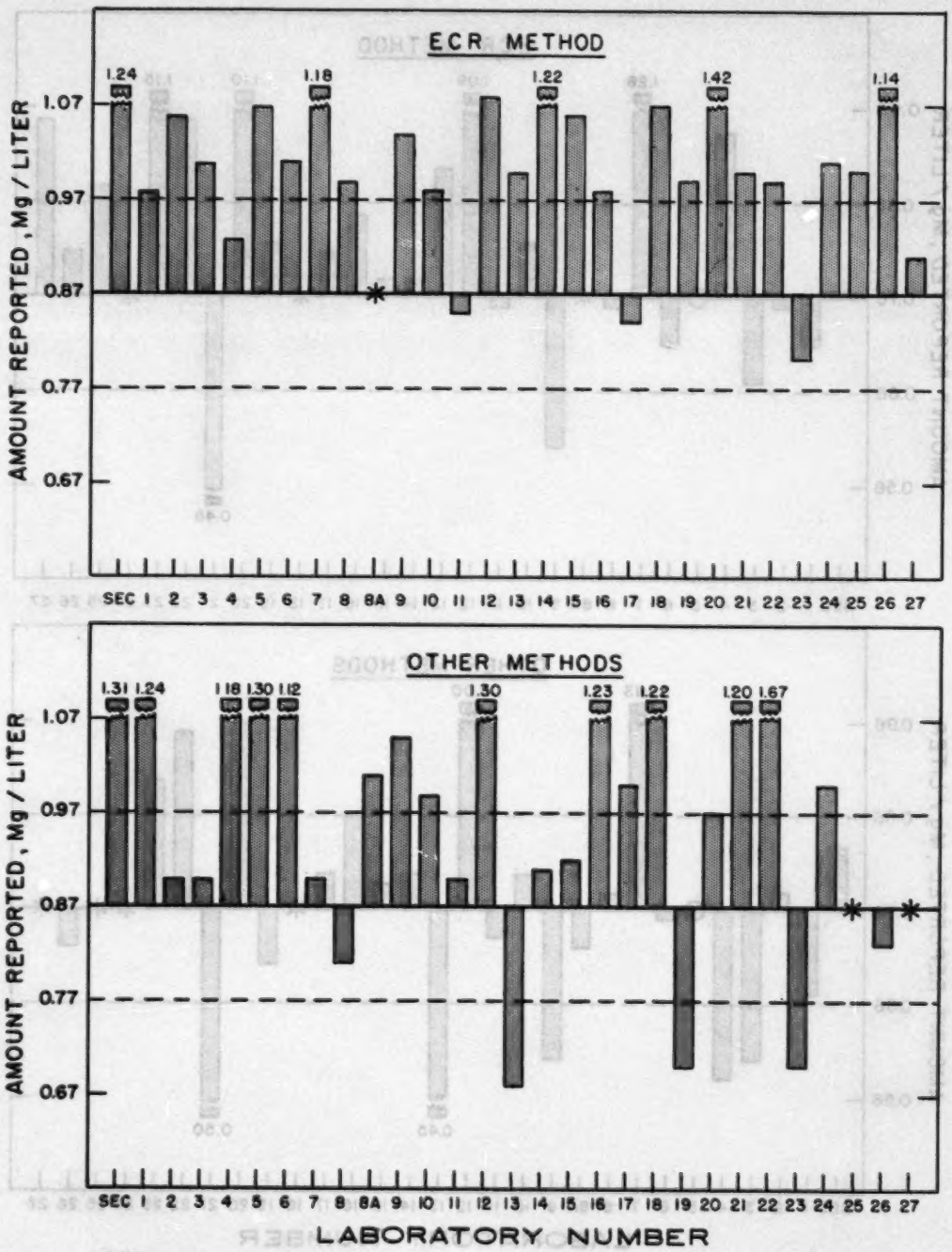
NOTE:

○ = PERFECT RESULTS

✱ = NO ANALYSIS PERFORMED

SOLUTION "C"-NON DISTILLED

CONTAINING 200 MG/L SULFATE, 2.5 MG/L $[NaPO_3]_6$



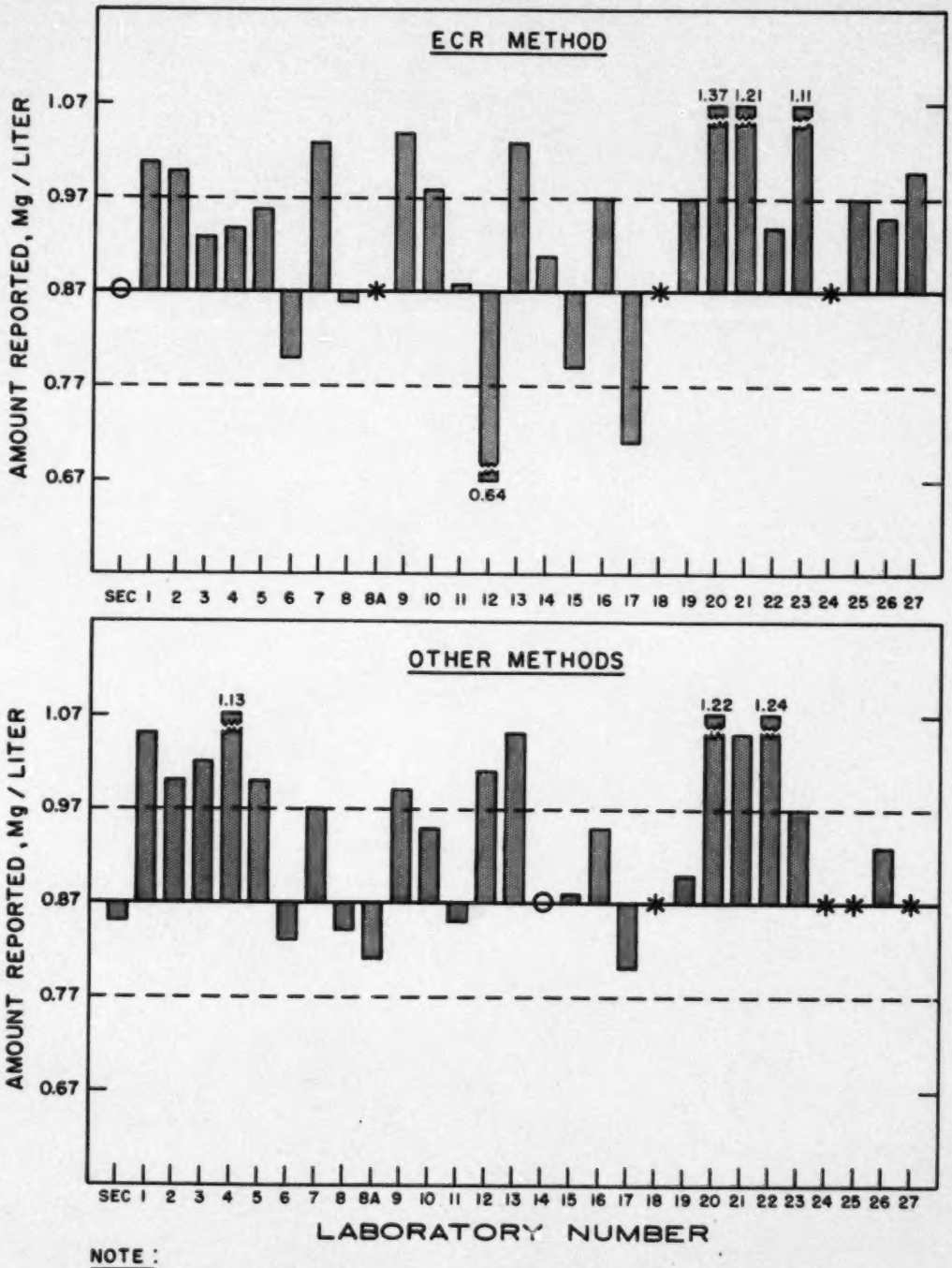
NOTE:

○ = PERFECT RESULTS

✱ = NO ANALYSIS PERFORMED

SOLUTION "C"-DISTILLED

CONTAINING 200 MG/L SULFATE, 2.5 MG/L $[NaPO_3]_6$



NOTE:

○ = PERFECT RESULTS

✱ = NO ANALYSIS PERFORMED